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UTILITY APPLICATION FOR UNITED STATES LETTERS PATENT
FOR
METHOD OF MAKING AND USING NANOSCALE METAL

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This application claims the benefit of U.S. Provisional Application No. 60/257,917 filed December 21, 2000. The entirety of U.S. Provisional Application No. 60/257,917 is hereby incorporated by reference.

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BACKGROUND AND SUMMARY OF THE INVENTION

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Since the mid-1990's, there have been a series of dramatic developments for the in-situ treatment of chlorinated solvents. The approach of the present invention is based on the sequential reduction of chlorinated hydrocarbons to innocuous end products such as methane, ethane or ethene. In principal the process has been recognized in scientific circles but, it is just beginning to be investigated for environmental application. The process exploits the use of zero valence state elemental metals to reductively dehalogenate halogenated hydrocarbons. In addition, elemental metals may be used to reduce soluble metals such as chromate to insoluble species (Cr (III)) or metalloids such as arsenic or selenium.

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The most common metal being utilized for this purpose is iron. But other metals including tin, zinc, and palladium have also shown to be effective. The process may be best described as anaerobic corrosion of the metal by the chlorinated hydrocarbon. During this process, the hydrocarbon is adsorbed directly to the metal surface where the dehalogenation reactions occur. Increasing surface area (by reducing the size of iron particles) increases the effectiveness of the process.

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The variations of the process are complex. Recent research on iron systems indicates three mechanisms at work in the reductive process.

- Metallic iron may act as a reductant by supplying electrons directly from the metal surface to the adsorbed halogenated compound.
- 5 • Metallic iron may act as a catalyst for the reaction of hydrogen with the halogenated hydrocarbon. The hydrogen is produced on the surface of the iron metal as the result of corrosion with water.
- Also ferrous iron solubilized from the iron metal due the above reactions may act as a reductant for the dehalogenation of halogenated hydrocarbons.

10 The rate of the reaction of the metallic iron with halogenated hydrocarbons has been demonstrated to be partially dependent upon the surface area of the metallic iron. As the size of the metallic iron is reduced, surface area goes up as well as chemical reactivity. Initial applications of this technology used iron filings. More recent applications have used iron colloids in the micron size range. The applications of the
15 metallic iron reduction of the present invention incorporate nanoscale colloids. These are colloids that range in size from 1 to 999 nanometers. A colloid of this size may have several advantages in application for in-situ groundwater treatment or for use in above ground treatment reactors. These advantages include:

- High surface area with greater reaction kinetics as a result. The increase in kinetics
20 allows for a lower mass loading of iron in the treatment zone or reactor because the residence time required for complete dehalogenation is decreased.
- The small size and greater reactivity of the colloid allows for the application of the technology through direct in-situ injection into the subsurface.

- The smaller size allows for advective colloidal transport.
- The greater reactivity, due to the small size, allows for much lower overall iron mass requirements.

To further enhance the physical and chemical character of the colloid, a metallic catalyst may be used to create a bi-metallic colloid. The catalyst further increases the rates of reactions, which further lowers the amount of iron colloid that must be used to create an effective reductive dehalogenation treatment zone in the subsurface or a surface reactor. Metals that may be used as a catalyst with the iron include palladium, platinum, nickel, zinc, and tin.

10 PRODUCTION OF NANO-SCALE IRON COLLOIDS

Introduction

A key limitation on the development of the technology of the present invention is the lack of availability of nanoscale metallic colloids. Research, driven primarily by the materials science needs (hi-tech electronic chips or component industry products), has, over the last decade, contributed to general technologies designed to produce nanoscale colloids. Although, generally the research has been in the area of colloids that are composed of ceramic or other non-metallic inorganic materials and not metal colloids. A significant part of the development effort for the technology of the present invention was the adaptation of the non-metallic nanoscale colloid production methods to the production of metallic nanoscale colloids of the present invention.

The method for the production of metal colloids in the nanoscale range may be divided into two primary approaches:

- "Bottom Up" in which colloids of the appropriate size are produced by being assembled from individual atoms.
- "Top Down" in which colloids of the appropriate size are produced by attrition of larger existing particles of the metal.

5 The "Bottom Up" approach has a greater number of potentially applicable methods, including:

- Chemical reduction using sodium borohydride; various soluble metal salts (such as ferrous or ferric chloride for iron) in suspensions of water or various hydrocarbon solvents. This process may or may not be enhanced with sonofication during reaction processes.
- Other chemical precipitation reactions in aqueous or hydrocarbon solutions capable of producing metals from soluble salts that may or may not include sonofication during reaction processes.
- Various methods of metal volatilization and subsequent deposition, typically under vacuum. These include:
 - Gas Evaporation
 - Active Hydrogen-Molten Metal Reactions
 - Sputtering
 - Vacuum Evaporation to Running Oil Surface
 - Evaporation Using Direct Electrical Current Heating
 - Hybrid Plasmas

20 The "Top Down" approach uses two primary variations of milling or mechanical comminution, this includes:

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- Using mechanical agitation of a mixture of the desired colloidal metal, a grinding media, and an organic or aqueous suspension fluid. Examples include ball mills and rod mills.
 - Systems similar to the above where the mechanical agitation is provided by high-speed gas jets.

Upon searching for a supply of nanoscale colloids the inventors of the present invention found that the only method of production capable of producing nanoscale colloids in large kilogram amounts was the sodium borohydride reduction method. However, this was expensive (up to \$5,000 per kilogram) and not practical for full-scale application of the technology.

After an evaluation of other production methods the following determinations were made:

- Metal volatilization was also expensive, the reactors available for the production of colloids were limited to kilogram capacities, and the colloids produced are at the lower end of the nanoscale range (typically less than 10 nanometers). With time and further development these technologies may also be applied to the production of nanoscale iron colloids for environmental use.
- "Top Down" mechanical attrition had the potential of:
 - Generating colloids of the proper size
 - Colloid production at a reasonable cost (\$100 a kilogram or less)
 - Production capacity in the 100 to 1000 kilogram range.

However, at the time of the evaluation there was no existing capacity (of any size) for the production of iron colloids using mechanical attrition. All work in the field was

being performed on ceramics or other non-metallic inorganic materials. The inventors of the present invention sought a provider of nanoscale ceramic production and generated the specifications and requirements for the production of nanoscale iron colloids.

Production of Nanoscale Colloids by Mechanical Attrition

5 Nanoscale colloids have been produced in amounts up to 10 kilograms, with scale-up production volumes readily and cost effectively available. The process developed to date includes the following components:

- Feed material consisting of approximately <325 mesh sized iron particles.
- Organic suspension solvent fluids that:
 - 10 • Have high flash points to prevent explosions; and
 - Are not reactive to the surface of the iron colloid
 - Examples may include dodecane, butyl acetate, and polypropylene glycol ethyl ether acetate
 - Dispersants to act as surface acting agents to prevent the agglomeration of the
 - 15 colloids during the milling process were used.
 - Examples include SOLSPERSE[®] 20,000, SOLSPERSE[®] 24,000, SOLSPERSE[®] 32,600, SOLSPERSE[®] 32,500, DISPERBYK[®] 108, DISPERBYK[®] 164, and DISPERBYK[®] 167.
- The materials are placed in a high energy ball milling system that is capable of using
- 20 grinding media as small as 0.2 mm
- Rate of agitation and time of milling are further parameters that are used to control generation of a nanoscale iron colloid of the desired properties. Lower energy milling

is used initially to insure proper mixing of the solvent, dispersion, and iron components.

PRODUCTION METHOD EFFECTS ON COLLOID MORPHOLOGY

- Each of the production methods described above produce colloids that have distinct morphology and internal crystal structure. In addition, it is important to recognize that in the nanoscale range quantum size effects begin to become apparent. For example a colloid of 10 nanometer diameter has about 30% of its atoms in grain boundaries (which are highly reactive and subject to quantum effects). These features may have an effect on the physical/chemical behavior of the colloid in use. These effects fall into two broad categories that reflect on production by "Bottom Up" or "Top Down" methods.
- A colloid produced by chemical precipitation or reduction, or through the various vapor deposition methods may be nano-structured. This means that the colloid may have nanoscale crystal domains with sharp boundaries between crystals. The grain boundaries are typically only 1 atom thick and there is low dislocation density in the crystal structures.
 - The reactivity of a colloid of this type may be controlled primarily through the selection of an appropriate overall colloid size and resulting surface area. Smaller size means greater surface area and reactivity; larger size means lower surface area and reactivity.
 - A colloid produced by mechanical attrition may be nano-crystalline. The crystal domains in the colloid are, relative to the overall colloid size, small. The individual crystal domains are separated by wide amorphous transition regions that exhibit a

very high dislocation density. These transition regions may be as large as the crystal domains, but are still termed grain boundaries.

- The amorphous transition regions may be highly reactive. The size and intensity of dislocation density of the amorphous boundary regions rather than the absolute size of the colloid may dominate the reactivity of the colloid. A relatively large colloid produced by this method may have the same or greater reactivity than a much smaller colloid produced by "Bottom Up" methods.

Control of the reactivity of the colloid is a critical feature. The iron undergoes anaerobic corrosion when reacted directly with halogenated solvents or when reacted with water to produce hydrogen. As the reactivity of the colloid increases the hydrogen production rate increases as well. By controlling the rate of hydrogen production using the methods described above, one may design reactive metal colloids with reactivity that will generate hydrogen at the rate required for the desired dehalogenation processes rather than at excessively higher rates (with just water) at which the iron colloid would be consumed (by the water) without reacting with the halogenated solvents undergoing treatment. Control of this type is particularly important for in-situ applications.

Important factors in the control of the colloid morphology using chemical precipitation include:

- Concentration of reagents
- Variations in the composition of the metal salt used as a feed material
- Composition of the suspending solvents
- Composition of the reducing agent
- Temperature at which the reactions take place

- The use and energy of mechanical agitation including sonofication.

Important factors in the control of the colloid morphology using vapor deposition methods include:

- Temperature of vaporization reactor
- 5 • Temperature in the deposition/collector zone
- Composition of metal (effects of alloying in addition to elemental composition)
- Composition of coating fluids in the collector
- Rate of deposition

10 Important factors in the control of the colloid morphology using mechanical attrition include:

- Composition of metal (alloy effects as well elemental composition)
- Type and concentration of suspending solvent
- Type and concentration of dispersion agent
- Size and shape of metal feed stock particles (and concentration in suspension)
- 15 • Size and shape of grinding media (and amount in suspension)
- Energy/rate of ball milling
- Time of milling
- If gas agitation is used:
 - Gas composition
 - 20 • Gas pressure, flow rate and configuration of injection system.

Post production processes may also impact colloid morphology and crystal structure, these post production processes include:

- Annealing

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- To various temperatures ranging from room temperature to the melting point of the colloid
 - At various heating rates and total annealing times
 - In the presence of various gases
 - 5 • Treatment with other aqueous or organic solutions
 - Drying processes including:
 - The use of heat
 - The use of evaporation
 - Vacuum drying
 - 10 • The composition of the blanketing gas used during the drying process.

Through the manipulation of the colloid size, morphology, and crystal structure using the above process it is possible to design colloids for variations in specific contaminant types, concentrations, groundwater or reactor flow velocities, subsurface permeability, and provide some control over the transport properties of the colloids during injection.

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BRIEF DESCRIPTION OF THE DRAWINGS

In addition to the novel features and advantages mentioned above, other objects and advantages of the present invention will be readily apparent from the following descriptions of the drawings and preferred embodiments, wherein:

20 Figure 1 is a schematic view of one preferred embodiment of the present invention.

Figure 2 is a schematic view of one preferred embodiment of the present invention.

Figure 3 is a schematic view of one preferred embodiment of the present invention.

Figure 4 is a schematic view of one preferred embodiment of the present invention.

5 Figure 5 is a flow-chart of one preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 Figure 1 illustrates a method of the present invention **10** for injecting the nanoscale metal **26** of the present invention by pump **20** through an injector **22** into a open bore hole **12** through a screen **16** into a plume **24** that is located beneath ground level **18** and beneath the water table **14**.

15 Figure 2 illustrates another method of the present invention **30** for injecting the nanoscale metal **46** of the present invention by pump **40** through an injector **42** into a open bore hole **32** through a screen **36** into a plume **44** that is located beneath ground level **38** and beneath the water table **34**. Non-contaminated water **48** beneath the water table is also illustrated.

20 Figure 3 shows another embodiment of a method of the present invention **50** for injecting nanoscale metal **68** of the present invention through an injector **62** through a screen **52** into a plume **64** that is located beneath ground level **58** and above or near the water table **54** with the use of an auger **66** for mixing the soil and a dust or vapor collector **72** for removing the dust through a removal pipe **70**. Non-contaminated water **56** beneath the water table **54** is also illustrated.

Figure 4 shows another embodiment of a method of the present invention **80** for

injecting the nanoscale metal 96 of the present invention by pump 90 through an injector 92 into a open bore hole 82 through a screen 86 into soil beneath ground level 88 and beneath the water table 84 with the use of hydraulic pressure 98 for fracturing the soil 94. The hydraulic pressure 98 is used to fracture the soil 94 and the nanoscale metal 96 is
5 injected either simultaneously or after the hydraulic pressure 98 has been applied.

Figure 5 is a flow chart that explains the process of producing the nanoscale metal.

The present invention is a method of producing nanoscale metallic colloids comprising the steps of:

- 10 a. supplying an elemental metal, wherein the size of the elemental metal is in the range of 1-10 microns;
- b. suspending the elemental metal in a non-aqueous organic liquid that is non-reactive to the surface of the elemental metal;
- c. adding a dispersant;
- 15 d. placing the materials in a ball milling system; and
- e. agitating the mixture at a rate and time necessary to produce nanoscale particles of product material.

Elemental metal is any metal in its elemental state having a zero valence. Metals that are preferred are selected from the group of iron, tin, zinc and palladium. The most
20 preferred is iron. The elemental metal is initially introduced in the size range of 1-10 microns and is most preferably 325 mesh metal particles.

The elemental metal may additionally be mixed with a second metal. Any metal may be used for the bi-metallic colloid but preferred metals are palladium, platinum, nickel,

zinc and tin.

The non-aqueous organic liquid is any liquid that will not react with the surface of the metal and preferably has a high flash point to prevent explosions. The non-aqueous organic liquid is preferably selected from the group consisting of dodecane, butyl acetate and polypropylene glycol ethyl ether acetate and mixtures thereof.

Dispersants are any surface acting agent used to prevent agglomeration of the colloids during the milling process. They are preferably selected from the group consisting of SOLSPERSE[®] 20,000, SOLSPERSE[®] 24,000, SOLSPERSE[®] 32,600, SOLSPERSE[®] 32,500, DISPERBYK[®] 108, DISPERBYK[®] 164 and DISPERBYK[®] 167 (SOLSPERSE[®] dispersants available from Avecia Limited, Manchester, UK and DISPERBYK[®] dispersants available from BYK-Chemie GmbH, Wesel, Germany).

The product material, also called nanoscale metallic colloids, is in the size of approximately 100-400 nanograms.

Comminuation of the metal particles, the non-aqueous organic liquid and the dispersant may be accomplished by any known milling or mechanical comminuation means or any system where the mechanical agitation is provided by high speed gas jets. Preferably ball milling or rod milling is used.

Additionally, the present invention is to a method of injecting nanoscale metal particles into soil, comprising the steps of:

- a. making a colloid suspension having metal particles in the presence of a carbohydrate; and
- b. injecting said colloid suspension into the soil through a well at a flow rate sufficient to move the colloid suspension through the soil.

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The nanoscale metal particles may be injected by any known method but are preferably injected under pressure (without the use of surfactants) or injected with hydraulic pressure. Most preferably, nitrogen under pressure will be used. The elemental metal or bimetallic colloid may be used alone or may be suspended in the nitrogen gas and may be mixed with a carbohydrate solution (also called carrier). Alternatively, the carbohydrate solution may be in atomized form and may be injected into the compressed nitrogen gas. The injection may also be achieved with the use of hydraulic pressure in which a slurry of elemental metal or bimetallic colloid and carbohydrate solution are injected. Additionally, sand may also be added to the slurry.

Any carbohydrate solution that creates an oxygen-scavenging environment may be mixed with the metal. Most preferably, corn syrup may be used in suspension with nanoscale metal and injected by pressure into a contaminated sub-soil zone. The corn syrup helps to prevent elemental iron from rusting which would have the effect of lessening the remediation capability of the iron.

The scope of the invention is not to be considered limited by the above disclosure, and modifications are possible without departing from the spirit of the invention.